

Ultrasonic Measurement of the Elastic Constants of Anthracene*

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Measurements have been made of the ultrasonic velocities for 18 modes of propagation in single-crystal anthracene. The accuracy of the measurements was limited by high attenuation, small specimen size, and inhomogeneities in the material. Approximate values are deduced for all 13 elastic constants. The results are compared with those obtained by other investigators for naphthalene. A revised treatment of the data reduction for the latter is presented.

Although the organic phosphors have been extensively investigated in regard to their electronic structure there has been very little work done on their elastic properties. Information on the latter has value, not only for its own sake, but also for the bearing it might have on the understanding of optical phenomena such as the indirect transitions and the diffusion of triplet excitons. Monoclinic structure characterizes anthracene and naphthalene, two of the best known of materials in this class. For naphthalene a complete determination of all elastic constants has been carried out by Aleksandrov *et al.*¹

Like the work of Aleksandrov *et al.* our investigation on anthracene used the standard pulsed ultrasonic methods² to determine the acoustic velocities and hence the stiffness moduli. The techniques and results evolved in the course of two studies carried out sequentially by the junior authors in obtaining their M.S. degrees. The problem is fairly complex since the crystal classes of the monoclinic system are characterized by 13 independent elastic constants as a result of the low symmetry. The acoustic measurements require a quite complicated analysis to yield the elastic constants.

Anthracene is a colorless organic solid obtained from coal tar which melts 214°–218°C and has a density of 1.25 g/cc. It is slightly soluble in alcohol, benzene, carbon disulfide, ether, and chloroform.^{3,4}

The bulk of the measurements were carried out on specimens purchased from Harshaw Chemical Company, two $\frac{1}{2}$ -in. cubes and one cylindrical disk a $\frac{1}{2}$ in. in diameter and $\frac{1}{2}$ in. thick. We were, however, fortunate in receiving specimens supplied to us from two other

sources. G. J. Sloan of the Dupont Central Research Laboratory gave us several $\frac{1}{4}$ -in. cylindrical disks with the parallel cleavage surfaces at about 115° to the cylindrical side surfaces. From R. C. Jarnagin of the Chemistry Department at the University of North Carolina we also received several very carefully prepared specimens mostly in the form of thin slabs.

The usual Voigt notation for elastic crystal constants refers to a Cartesian coordinate system rather than the Bravais lattice of the crystal. Our convention was to choose Cartesian axes x_1 and x_2 to be parallel, respectively, to lattice translations a and b (where b is the monoclinic axis perpendicular to a and c , and a and c make an angle of 124.7°, as shown in Fig. 1). The x_3 Cartesian axis is perpendicular to the cleavage (a - b) plane. Indices that appear throughout refer to this Cartesian system.

EXPERIMENTAL PROCEDURE

The crystal blanks were oriented by the usual Laue back-reflection. Cleavage planes where exposed could be identified immediately and where not apparent could sometimes be revealed by judicious cleaving of a corner or edge. Otherwise the procedure began with the identification of the reflection plane coming from the projection of the a - c plane and involved a rather lengthy series of rotation to bring the crystal cleavage face perpendicular to the x-ray beam.

From the exposures of the cleavage plane the direction of the b axis was easily identified by its reflection symmetry. Three or four rather strong spots appearing on the a axis were used to determine its sense. The angular precision corresponding to these points was insufficient to establish unequivocally to which planes they should be attributed. Identification was finally made possible with the help of a nickel filter following a copper target, so that only those spots which roughly satisfied the Bragg condition were retained.

To prepare the specimen for ultrasonic propagation along prescribed directions, a straightforward cutting procedure was used to reveal any required parallel planes. The cutting was carefully performed with a guided razor blade. The surfaces were subsequently polished, etched with ethyl alcohol, and x rayed to check on final orientation. The Harshaw cylinder with a

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¹ K. S. Aleksandrov, G. S. Belikova, A. P. Ryzhenkov, V. R. Teslenko, and A. I. Kitaigorodskii, *Kristallografiya* 8, 221 (1963) [*Sov. Phys.—Crystallogr.* 8, 164 (1963)].

² H. B. Huntington, *Phys. Rev.* 72, 321 (1947).

³ J. M. Robertson, *Organic Crystals and Molecules* (Cornell University Press, Ithaca, N.Y., 1952).

⁴ *Handbook of Chemistry and Physics* (Chemical Rubber Publ. Co., Cleveland, Ohio, 1948) 30th ed., p. 626.

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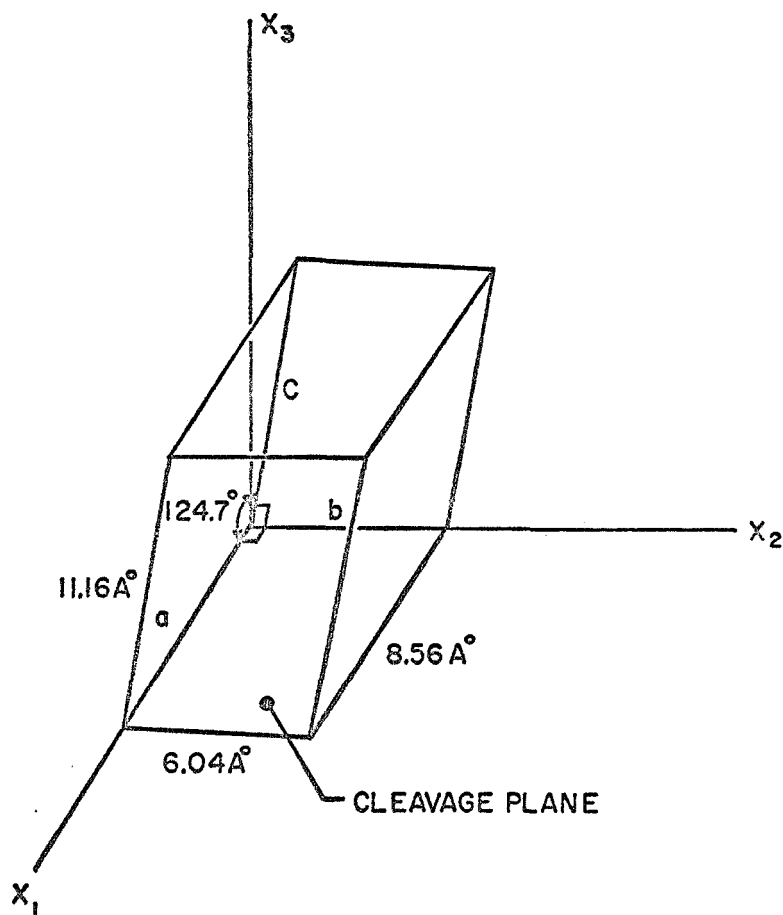
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FIG. 1. Anthracene crystal cell dimensions and Cartesian coordinate system.



$\frac{1}{2}$ in. between the cleavage planes was cut into a rectangular parallelepiped with planes perpendicular to the $[100]$ and $[010]$ directions. Another Harshaw specimen was shaped to give $[10\bar{1}]$ propagation (referred to the Cartesian system). An accuracy of $\pm 1^\circ$ for these 45° cut was found possible. Attenuation of the transverse beams in the 3 direction was very high, independent of source of the specimen. All crystals were annealed for 2 h at 140°C and then allowed to furnace cool overnight.

The ultrasonic procedure was to use 10-Mc/sec pulsed propagation at room temperature. The pulsed oscillator, attenuators, and wide-band amplifiers were all the standard items produced by the Arenberg Ultrasonic Laboratory. The rectified video pulses were timed directly on a Tektronix 545A oscilloscope. For transducers, X- and Y-cut quartz crystals were used for longitudinal and transverse excitation, respectively. For bonding agents Nonaq stopcock grease (for longitudinal waves only) and Salol were used.

For the measurement itself each echo was brought to the same level on the scope by use of the attenuator, and the ranging blip was set in turn on the leading and falling edges of the first few echoes. The rapid course of the pulse deterioration limited observation in most

cases to two to four echoes. The measurements for many of the 45° cuts were handicapped by the small areas that were available for bonding with the transducer after shaping. Consequently the insertion losses were large and the signals had to compete with the trailing edge of the main bang. The larger specimens from the commercial supplier showed small cracks and optical inhomogeneities. The material also generally exhibited high attenuation, although this could be mitigated somewhat by careful annealing. For all these reasons the velocity measurements had only a marginal accuracy, at best about 2%, often considerably worse. The greatest single source of error arose from the "so-called" transit time correction which is involved in any form of direct echo ranging. (This difficulty could have been avoided by using the available ultrasonic interferometer,⁵ had the pulse shape been good enough to permit this technique.)

The transit time correction was first reported by Lazarus⁶ who observed that the direct measurement of the video pulse position on a scope time base involved a correction for pulse deterioration caused by each

⁵ J. Williams and J. L. Lamb, *J. Acoust. Soc. Am.* **30**, 308 (1958); Z.-P. Chang, *Phys. Rev.* **140**, A1788 (1965).

⁶ D. Lazarus, *Phys. Rev.* **76**, 545 (1949).

reflection at the transducer. The nature of the effect was later analyzed by Eros and Reitz.⁷ One can attempt to correct for this experimentally by comparing specimens of different length or by finding the extra delay caused by adding a second transducer on the end opposite to the first transducer. Following the latter procedure gave corrections of 0.2–0.4 μsec but the process was laborious and gave erratic results. Lange⁸ has treated this problem analytically using the frequency transform approach. Neglecting the influence of piezoelectric absorption and the effect of the bonding element, he arrives at the following simple formula at resonance. $\tau_t = (Z_t/Z_s)(2l/v_s)$ for the transit time correction where Z_t is the acoustic impedance of the transducer and Z_s that for the specimen. The quartz crystal acts as a high Q resonance whose ringing prolongs the pulse. Accordingly we decided to use this formula to compute our correction factors rather than rely on somewhat erratic measurements. The data as a whole hardly seemed to justify greater pains.

The results of the velocity measurements are given in Table I. They comprise a longitudinal and two transverse values for each of six directions, three, respectively parallel to the Cartesian axes and three at 45° to these axes. The first column gives the ordinal number by which that particular propagation will be designated henceforth. The second and third column give, respectively, the directions of propagation and polarization. The next two columns give the specimen thickness and number of echoes recorded. The sixth column gives the measured velocities and the final column ρv^2 in 10^{11} dyn/cm². The nominal density was taken to be 1.25 g/cm³.

DATA REDUCTION

The process of finding the 13 elastic constants from the 18 listed ρv^2 values involves the analysis of solving the Christoffel equations for each of six orientations. The appropriate secular determinants for each case are given below:

$$\begin{vmatrix} c_{11}-\rho v^2 & c_{15} & 0 \\ c_{15} & c_{55}-\rho v^2 & 0 \\ 0 & 0 & c_{66}-\rho v^2 \end{vmatrix}, \quad \begin{vmatrix} c_{22}-\rho v^2 & 0 & 0 \\ 0 & c_{44}-\rho v^2 & c_{46} \\ 0 & c_{46} & c_{66}-\rho v^2 \end{vmatrix}, \quad \begin{vmatrix} c_{33}-\rho v^2 & 0 & c_{35} \\ 0 & c_{44}-\rho v^2 & 0 \\ c_{35} & 0 & c_{55}-\rho v^2 \end{vmatrix},$$

$$\begin{vmatrix} c_{22}'-\rho v^2 & c_{24}' & c_{26}' \\ c_{24}' & c_{44}'-\rho v^2 & c_{46}' \\ c_{26}' & c_{46}' & c_{66}'-\rho v^2 \end{vmatrix}, \quad \begin{vmatrix} c_{11}''-\rho v^2 & c_{15}'' & 0 \\ c_{15}'' & c_{55}''-\rho v^2 & 0 \\ 0 & 0 & c_{66}''-\rho v^2 \end{vmatrix}, \quad \begin{vmatrix} c_{22}'''-\rho v^2 & c_{24}''' & c_{26}''' \\ c_{24}''' & c_{44}'''-\rho v^2 & c_{46}''' \\ c_{26}''' & c_{46}''' & c_{66}'''-\rho v^2 \end{vmatrix}.$$

The primed elastic constants for the rotated systems can be expressed in terms of the unrotated constants as follows:

For 45° rotation about $[100]$,

$$\begin{aligned} c_{22}' &= \frac{1}{4}(c_{22}+c_{33}+2c_{23}+4c_{44}), & c_{44}' &= \frac{1}{4}(c_{22}+c_{33}-2c_{23}), \\ c_{66}' &= \frac{1}{2}(c_{55}+c_{66}), & c_{24}' &= \frac{1}{4}(c_{33}-c_{22}), & c_{26}' &= (2\sqrt{2})^{-1}(c_{25}+c_{35}+2c_{46}), \\ c_{46}' &= (2\sqrt{2})^{-1}(c_{35}-c_{25}). \end{aligned}$$

For 45° rotation about $[010]$ to propagate in $[10\bar{1}]$ direction,

$$\begin{aligned} c_{11}'' &= \frac{1}{4}(c_{11}+c_{33}-2c_{13}-4c_{35}+4c_{55}), & c_{55}'' &= \frac{1}{4}(c_{11}+c_{33}-2c_{13}), \\ c_{66}'' &= \frac{1}{2}(c_{44}+c_{66}+2c_{46}), & c_{15}'' &= \frac{1}{4}(c_{11}-c_{33}+2c_{35}-2c_{15}). \end{aligned}$$

For 45° rotation about $[001]$,

$$\begin{aligned} c_{22}''' &= \frac{1}{4}(c_{11}+c_{22}+2c_{12}+4c_{66}), & c_{44}''' &= \frac{1}{2}(c_{44}+c_{55}), & c_{66}''' &= \frac{1}{4}(c_{11}+c_{22}-2c_{12}), \\ c_{24}''' &= -(2\sqrt{2})^{-1}(c_{25}+c_{15}+2c_{46}), & c_{26}''' &= \frac{1}{4}(c_{22}-c_{11}), & c_{46}''' &= (2\sqrt{2})^{-1}(c_{15}-c_{25}). \end{aligned}$$

Of the six secular determinants above four can be decomposed into a linear and a quadratic solution each. In the first stage of the analysis, the four linear solu-

tions serve to give four constants directly and uniquely,

$$F_2 = c_{66} = 0.42; \quad F_4 = c_{22} = 1.16;$$

$$F_9 = c_{44} = 0.27; \quad F_{14} - \frac{1}{2}(F_2 + F_9) = c_{46} = -0.13, \quad (1)$$

all in units of 10^{11} dyn/cm² as will be henceforth understood. Here F stands for ρv^2 and the subscript gives the

⁷ S. Eros and J. R. Reitz, J. Appl. Phys. 29, 683 (1958).

⁸ J. N. Lange, J. Acous. Soc. Am. 40, 998 (1966).

ELASTIC CONSTANTS OF ANTHRACENE

TABLE I. Measured ultrasonic velocities in anthracene.

No.	Direction of propagation	Direction of polarization	Thickness (in.)	No. of echoes	Velocity in 10^3 cm/sec	ρv^2 in 10^{11} dyn/cm ²
1	100	100	0.237	4	2.71	0.92
2	100	010	0.237	2	1.84	0.42
3	100	001	0.237	3	1.16	0.17
4	010	010	0.284	4	3.05	1.16
5	010	001	0.284	2	1.28	0.20
6	010	100	0.284	3	2.01	0.50
7	001	001	0.110	7	3.73	1.74
8	001	100	0.110	3	1.65	0.34
9	001	010	0.104	2	1.47	0.27
10	011	011	0.183	5	3.11	1.21
11	011	100	0.183	3	2.00	0.50
12	011	01 $\bar{1}$	0.183	2	1.35	0.23
13	10 $\bar{1}$	10 $\bar{1}$	0.121	5	3.20	1.28
14	10 $\bar{1}$	010	0.121	4	1.34	0.22
15	10 $\bar{1}$	101	0.121	3	1.10	0.15
16	110	110	0.218	4	3.12	1.22
17	110	001	0.218	2	1.39	0.24
18	110	1 $\bar{1}$ 0	0.218	2	1.21	0.18

ordinal index. These results from the pure mode propagations are more accurate than the remaining evaluations. At this point we can use the trace relations from the quadratic and cubic equations to supply four cross checks,

$$F_5 + F_6 = F_2 + F_9 \quad \text{gives } 0.71 \text{ vs } 0.69, \quad (2a)$$

$$F_9 + \frac{1}{2}(F_2 + F_4 + F_7 + F_8) = F_{16} + F_{11} + F_{12} \\ \text{gives } 2.09 \text{ vs } 1.94, \quad (2b)$$

$$F_2 + \frac{1}{2}(F_4 + F_9 + F_{11} + F_3) = F_{16} + F_{17} + F_{18} \\ \text{gives } 1.68 \text{ vs } 1.64, \quad (2c)$$

$$F_5 F_6 = F_2 F_9 - [F_{14} - \frac{1}{2}(F_2 + F_9)]^2 \\ \text{gives } 1.00 \text{ vs } 0.97. \quad (2d)$$

The extent to which these internal checks are verified gives a good index of the accuracy of the data.

The next step in the calculations involves more complicated algebra with a considerable opportunity for propagations of errors. From the following five equations one can derive a long quadratic equation for c_{55} :

$$c_{55} + c_{11} = F_1 + F_3; \quad c_{11}c_{55} - c_{15}^2 = F_1F_3; \quad (3a)$$

$$c_{55} + c_{33} = F_7 + F_8; \quad c_{33}c_{55} - c_{25}^2 = F_7F_8 \quad (3b)$$

$$-(c_{15} + c_{35}) = F_{13} + F_{15} - \frac{1}{2}(F_1 + F_3 + F_7 + F_8). \quad (3c)$$

The quadratic equation has the numerical solutions 0.58 and 0.36. The first value for c_{55} can be discarded since it would lead to $c_{55} > c_{11}$ and the identification of the No. 3 propagation with the pseudolongitudinal wave. Our additional information in the polarization of the various beams can be used to eliminate this possibility. Accordingly one can list values for five more constants,

$$c_{55} = 0.36, \quad c_{11} = 0.72, \quad c_{33} = 1.72, \quad c_{15} = 0.33,$$

and

$$c_{35} = -0.16, \quad (4)$$

One can now turn to the equation for the product of the roots of the quadratic, F_{13} and F_{15} ,

$$c_{11}''c_{55}'' - c_{15}''^2 = F_{13}F_{15}, \quad (5)$$

which involves c_{13} as an unknown in both of the factors of the first term. The resulting quadratic equation for c_{13} has roots 0.33 and -0.73 . Again the second root can be eliminated on the basis of additional information, i.e., that the fastest wave in the $[10\bar{1}]$ direction is pseudolongitudinal.

In the final stage of the analysis one attempts to determine c_{23} , c_{12} , and c_{25} from the equations for the roots of the two cubics. The trace relations have already been used but one can set the product of the roots equal to the determinant of the matrix and the sum of the pairwise

TABLE II. Listing the elastic constants.^a

	Anthracene		Naphthalene		
	Exptl ^b	Theoret ^c	Exptl ^d	Revision	Theoret ^c
c_{11}	0.72	0.79	0.78		0.68
c_{22}	1.16	1.31	0.99		1.13
c_{33}	1.72	1.67	1.19		1.74
c_{44}	0.27	0.31	0.33		0.47
c_{55}	0.36	0.46	0.21		0.31
c_{66}	0.42	0.25	0.42		0.27
c_{12}	~0.4	0.73	0.45	0.19	0.58
c_{13}	0.33	0.59	0.34		0.48
c_{15}	0.33	-0.02	-0.06		0.01
c_{23}	~0.8	0.56	0.23	-0.10	0.47
c_{25}	~0	0.14	-0.27	-0.35	0.13
c_{35}	-0.16	-0.49	0.29		-0.42
c_{46}	-0.13	0.10	-0.05	-0.07	0.03

^a All values in 10^{11} dyn/cm.^b This study.^c Reference 9.^d Reference 1.

products of the roots equal to the sum of the principal 2×2 minors. The matrix in this case has the general form,

$$\begin{array}{ccc} A+x & D & (B+y)/\sqrt{2}, \\ D & A-x & (B-y)/\sqrt{2}, \\ (B+y)/\sqrt{2} & (B-y)/\sqrt{2} & G, \end{array} \quad (6)$$

with the following notation:

$$x = \frac{1}{2}(c_{2i} + c_{jj}) \quad \text{and} \quad y = \frac{1}{2}(c_{25} + c_{46}), \quad (7a)$$

$$A = \frac{1}{2}c_{jj} + \frac{1}{4}(c_{22} + c_{ii}), \quad D = \frac{1}{4}(c_{ii} - c_{22}), \quad (7b)$$

$$B = \frac{1}{2}(c_{i5} + c_{46}) \quad \text{and} \quad G = \frac{1}{2}(c_{55} + c_{kk}). \quad (7c)$$

Here the varying indices i, j, k stand for 3, 4, and 6 when dealing with specimens rotated about the $[100]$ axis, and for 1, 6, and 4 when dealing with rotation about the $[001]$ axis. The equations in all cases describe conic sections. Those from the pairwise sum of the roots are circles and those from the products of the roots are canted ellipses. All figures are centered at the x, y origin, so that, if a solution in x and y exists, it is fourfold degenerate, i.e., the figures intersect at four points. This multiplicity can be reduced first by using polarization information as has been done earlier. Since negative values of x would interchange the roles of the pseudolongitudinal and pseudotransverse waves (polarized in the planes of rotation) these possibilities can be eliminated. Hopefully the remaining ambiguity can be removed by looking for solutions for y (or c_{25}) that agree between the results from propagation in the $[011]$ and $[110]$ directions.

Unfortunately for our particular data the circle lay just outside the ellipse for both the $[011]$ and the $[110]$ cases. Since no solution existed, it was not strictly possible to determine values for c_{12} , c_{23} , and c_{25} . Nevertheless as inspection of the geometry of the conic sections could serve to give quite a fair idea of the range into which each of these constants would fall if the data were changed enough to bring about an intersection. The ellipses are canted 25° - 35° in opposite directions from the x axis so that the common value for y must be near to zero (probably negative). Consequently c_{25} probably lies between 0.2 and -0.2 with a null average. From the dimensions of the ellipses in their long directions one deduces $c_{12} \sim 0.4$ and $c_{23} \sim 0.8$ with about the same uncertainty range. This completes the data reduction for determining the elastic constants. The values are listed in the first column of Table II.

DISCUSSION

A disturbing feature of the preceding data reduction is the failure to come up with real solutions for c_{12} , c_{23} , and c_{25} . It is natural to ask what sort of variations in the observed velocities would be needed to bring this feature into line. A rather careful investigation indicated that there was no trivial remedy. Corrections of about 15% would be needed for two or possibly three of the observed F values to resolve the difficulty. However, such errors might be expected from the transit time correction for longitudinal propagation in thin specimens, such as F_7 or F_{13} .

The lattice dynamics of these molecular crystals

have been attacked recently by Pawley⁹ using a model which regards the molecules as rigid and considers the intermolecular interaction to be the sum total of the two-body interactions between the atoms on adjacent molecules. For atomic interaction he chose the "6-exp" potential of Kitaigorodskii¹⁰ which has proved quite successful in obtaining the heat of sublimation and the lattice parameters for such crystals. The potential consists of an attractive van der Waals term and a repulsive exponential term with different constants according to whether the interaction is H-H, C-C, or C-H. This model has been applied to the calculation of the elastic constants for both anthracene and naphthalene and the results are listed in Columns 2 and 5 of Table II. A comparison between 1 and 2 shows a reasonable agreement between the largest of the diagonal constants and a general order-of-magnitude check elsewhere. It should perhaps be pointed out here that difficulty in determining the sense of the x axis, as described in the section on orientation, could lead to an ambiguity in the sign of the sum of c_{15} and c_{35} [Eq. (3c)] and hence in their signs individually since the other equations used in this evaluation (3) involve only the square of these constants. Moreover the relative error of this sum is large since the left hand of Eq. (3c) is the net of an 85% cancellation between larger terms.

As mentioned earlier there has been one prior investigation to determine the elastic constant of a monoclinic organic crystal, that of Aleksandrov *et al.*¹ on naphthalene. Their values are listed in Column 3 of Table II for comparison with the anthracene results. A reasonably close parallelism is evident for the diagonal elements and several of the nondiagonal elements. In spite of the low statistical spread in the data and the apparently high degree of internal consistency, the naphthalene results suffer from the serious defect that the determinant of the elastic constant 6×6 matrix is negative as was pointed out by Gordon.¹¹ Partly to seek an explanation of this difficulty and partly as a check for our data reduction procedure we decided to run the naphthalene numbers through the routine described earlier. The results bore out the excellent quality of the data. The internal checks of Eqs. (2a)–

(2d) were verified to within $1\frac{1}{2}\%$ in three out of the four relations. Our own experience¹² in working with naphthalene had shown that attenuation is less and the wave shape considerably sharper for ultrasonic propagation in this material than in anthracene. For the first two stages of the calculations there was a good check with the constants given by the Russian workers. However, the results for c_{12} , c_{23} , and c_{25} as obtained during the third stage from the simultaneous solutions between the circles and the canted ellipses came out quite differently. The new values are shown in the fourth column of Table II. The Russian workers give no details as to how they carried out the reduction of their experimental data, so that it is impossible to tell what is the origin of the disagreement. With the changes shown in Column 4 the determinant of the elastic constant matrix becomes positive and presumably the compliances could be obtained routinely. Incidentally Pawley⁹ has also re-evaluated the data reduction of Aleksandrov *et al.* but his revised results also fail to give a positive definite matrix for the elastic constants.

Even a rough determination of the elastic parameters of anthracene can be useful in several connections. Because the material is being studied intensively from many points of view information on the phonon properties can be of value. A group studying the behavior of the triplet exciton¹³ have had occasion to quote our preliminary results to show that the average diffusional velocity of the triplet is less than any acoustic velocity. Diffuse x-ray measurements¹⁴ have been used to explore some of the phonon frequencies. The comparison with theory⁹ has already proved to be interesting and informative.

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⁹ G. S. Pawley, *Phys. Status Solidi* **20**, 347 (1967).

¹⁰ A. I. Kitaigorodskii, *J. Phys. Chem.* **63**, 6 (1966).

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